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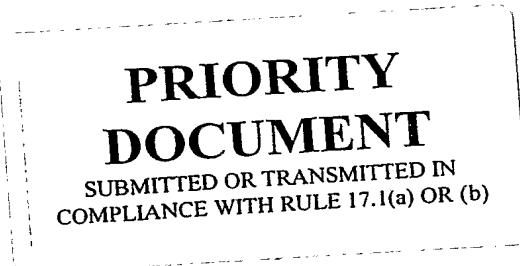
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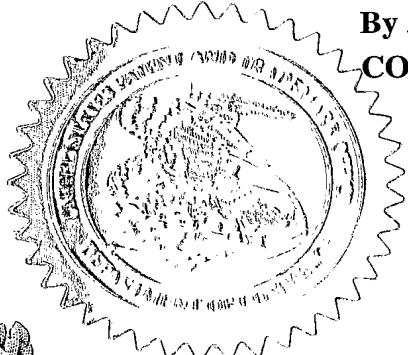
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By Authority of the
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T. WALLACE
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PATENT APPLICATION SERIAL NO. _____

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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ER573871996US

U.S. PTO
60550189**INVENTOR(S)**

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 Additional inventors are being named on the 1 separately numbered sheets attached hereto**TITLE OF THE INVENTION (500 characters max)****PROCESS FOR PREPARING POLYOLEFINS IN SUSPENSION**

Direct all correspondence to:

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ENCLOSED APPLICATION PARTS (check all that apply)

<input checked="" type="checkbox"/> Specification	Number of Pages	8	<input type="checkbox"/> CD(s), Number	
<input checked="" type="checkbox"/> Drawing(s)	Number of Sheets	5	<input type="checkbox"/> Other (specify)	
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76				

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.	FILING FEE AMOUNT (\$)
<input type="checkbox"/> A check or money order is enclosed to cover the filing fees	
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<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.	

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

 No. Yes, the name of the U.S. Government agency and the Government contract number are: _____

Respectfully submitted,

SIGNATURE William R. Reid

Date 03/03/2004

TYPED or PRINTED NAME William R. Reid

REGISTRATION NO.
(if appropriate)
Docket Number:

47,894

TELEPHONE 410-996-1783

FR 6162 (US)

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

PROVISIONAL APPLICATION COVER SHEET
Additional Page

PTO/SB/16 (02-01)

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Docket Number	FR 6162 (US)
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INVENTOR(S)/APPLICANT(S)

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Peter	Kölle	Bad Dürkheim, Germany

Number 2 of 2

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EXPRESS MAILING CERTIFICATE

This certifies that the attached **Form PTO/SB/16** (in duplicate), **Specification (8 pages)** and **5 Sheets of Drawings** for the provisional application of **Dr. Joachim Berthold et al.** for **PROCESS FOR PREPARING POLYOLEFINS IN SUSPENSION** (our ref: **FR 6162 (US)**) is being mailed by "Express Mail Post Office to Addressee" service in an envelope addressed:

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Alexandria, VA 22313-1450

and deposited on **MARCH 3, 2004** as "Express Mail" in the United States Postal Service, the number of the "Express Mail" mailing label being **ER573871996US**.

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PROCESS FOR PREPARING POLYOLEFINS IN SUSPENSION

The present invention relates to a continuous process for preparing polyolefins having a bimodal or multimodal molar mass distribution in suspension in at least two reactors which are connected in series and in which different reaction conditions are set.

5 In known processes for preparing polyolefins having a bimodal or multimodal molar mass distribution, monomers and hydrogen are firstly polymerized in the presence of a suspension medium and a suitable catalyst, preferably a Ziegler catalyst, in a first reactor under first reaction conditions and the reaction mixture is then transferred to a second reactor and polymerized further there under second reaction conditions, then, if desired, transferred to a
10 further reactor and there polymerized further under further reaction conditions, and so forth, with the first reaction conditions differing from the second and the further reaction conditions so that they lead to polyolefins having differing molar masses.

15 The total yield, based on monomer and comonomer used, in the known suspension polymerization processes is, as a function of an optimal polymerization formulation, in the range from 96 to 98%. An after-reactor which is installed downstream of the last polymerization stage and in which the output obtained from the individual polymerization stages is treated once again under reaction conditions enables the total yield to be increased further and brought to a value in the range from 98 to 99.5%.

20 However, an after-reactor always represents a considerable additional capital cost and it is particularly prone to malfunctions in operation, which is regarded as a serious drawback in industry.

25 It is therefore an object of the present invention to modify the known process of polymerization of olefins in suspension so that an after-reactor is avoided but a total yield, based on olefin monomer and comonomer used, of more than 98%, preferably more than 99%, can nevertheless be achieved in the polymerization.

30 This object is achieved by a process of the generic type mentioned at the outset in which the offgases leaving all the reactors connected in series are collected, the collected offgases are then compressed by means of a compressor, the compressed offgases are subsequently cooled and the cooled material is separated into a gaseous fraction and a liquid fraction and the separated fractions are then recirculated to the polymerization process at different points.

The collected offgases are preferably compressed to a pressure in the range from 0.5 to 2.5 MPa, preferably in the range from 0.9 to 2.0 MPa, and in the process heat up to temperatures in the range from 30 to 250°C. Compression of the offgases can be carried out by means of single-stage or multistage compression. In a multistage compression, cooling of the offgases can

5 be carried out after the individual stages.

The compressed offgases are subsequently cooled to a preferred temperature in the range from 0 to 100°C, particularly preferably in the range from 20 to 50°C. At a pressure in the range from 0.5 to 2.5 MPa, a liquid phase and a gaseous phase are then formed and these are collected in a vessel from which they can subsequently be taken off separately. Cooling of the compressed

10 offgases can also be effected by sprinkling with previously cooled liquid phase in a gas scrubber.

The polymerization process of the invention is preferably carried out in the presence of a Ziegler catalyst. The appropriate molar mass of the polymer fraction prepared in the various reactors is preferably set by addition of hydrogen to the reaction mixture. The polymerization process is preferably carried out so that the highest hydrogen concentration and the lowest

15 comonomer concentration, based on the amount of monomer, are set in the first reactor. In the downstream further reactors, the hydrogen concentration is gradually reduced and the comonomer concentration is altered, in each case once again based on the amount of monomer. Preference is given to using ethylene or propylene as monomer and an alpha-olefin having from 4 to 10 carbon atoms as comonomer.

20 Suitable suspension media are saturated hydrocarbons having from 4 to 12 carbon atoms and a mixture of these, which is also known as diesel oil.

Since the Ziegler catalyst generally suffers a decrease in its polymerization activity as the hydrogen concentration increases and because the suspension inevitably becomes increasingly diluted as the total conversion increases, the reacting polymer particles in the first reactor have

25 the longest mean residence time. For this reason, the highest conversion of the added monomer to homopolymer or of the added monomer and comonomer to copolymer is achieved in the first reactor, compared to the downstream reactors.

In the accompanying figures, the invention is illustrated by way of example.

Figure 1 shows a flow diagram of a multistage polymerization in a plurality of reactors

30 connected in series.

Figure 2A, 2B, 2C and 2D show individual flow diagrams for the offgas fractionation according to the invention.

In figure 1, the successive reactors R1, R2.x, R3.y and R4, where $x = 0, 1, 2, \dots$ and $y = 0, 1, 2, \dots$, are denoted by reference numerals. The reactors can, according to the invention, be
5 fill-level-regulated reactors in which the polymerization is carried out in a suspension medium at a pressure in the range from 0.01 to 1.6 MPa, at a temperature in the range from 60 to 120°C and with good mixing by means of a stirrer. The contents of the reactors can be cooled or heated via a jacket, which has been omitted in the schematic diagram. As an alternative, the reactors can be connected to one or more external cooling circuits (likewise not shown in the figure) in the
10 region of which the reactor contents which are being circulated by means of pumps are heated or cooled.

The contents of a reactor can be discharged directly through a regulatable valve, either continuously or discontinuously, into the next, downstream reactor or into the product work-up P when the pressure difference between the respective reactors or the product work-up P permits
15 this. However, the reaction mixture can also be discharged from one or more of the abovementioned external cooling circuits from the pressure side through a regulatable valve.

The reference numerals F1 and F2.x, where $x = 0, 1, 2, \dots$, denote fill-level-regulated intermediate vessels in which a defined pressure and a defined temperature prevail. These intermediate vessels F1 and F2.x serve to partly degas the reaction mixture. Hydrogen and inert
20 gases which, for example, go into solution from inert gas blanketing of stock vessels for suspension media or comonomers or are fed in as secondary constituents with the monomer or are formed by means of secondary reactions in the reactors R1 and R2.x can be removed in the intermediate vessels F1 and F2.x to make it possible for the reaction conditions in the polymerization in the downstream reactor R2.x and R3.y to be controlled precisely. The
25 intermediate vessels F1 and F2.x can be operated with or without a stirrer. The intermediate vessels F1 and F2.x can have a jacket for cooling or setting the temperature, but can also be connected to external cooling circuits.

The contents of the intermediate vessels F1 and F2.x can be discharged directly through a regulatable valve, either continuously or discontinuously, into the next, downstream reactors
30 R2.x and R3.y when the pressure difference between the respective intermediate vessel F1 and F2.x and the respective reactors R2.x and R3.y permits this. However, the reaction mixture can

also be discharged from one or more of the abovementioned pump-operated external cooling circuits from the pressure side through a regulatable valve.

The reference numerals E1, E2.x and E3.y, where $x = 0, 1, 2, \dots$, and $y = 1, 2, 3, \dots$, denote the streams into the reactors R1, R2.x and R3.y. The streams E1, E2.x and E3.y into the reactors R1, R2.x and R3.y are composed of difference proportions of suspension medium, catalyst, cocatalyst, monomer, comonomer, hydrogen and inert gases, with the proportion of one or more of the individual components also being able to be zero. The individual components of the streams E1, E2.x and E3.y can be fed individually or as a mixture, either continuously or discontinuously, into the reactors R1, R2.x and R3.y at one or more points via regulatable valves.

In figure 1, the reference numerals A1, A2.x, A3.y and A4, where $x = 0, 1, 2, \dots$ and $y = 0, 1, 2, \dots$, denote offgas streams which are branched continuously or discontinuously from the gas phases of the reactors R1, R2.x, R3.y and R4 via regulatable valves (not shown). The offgas lines, which are not shown in the figure, can additionally contain a cooling apparatus between the reactors R1, R2.x, R3.y and R4 and the regulatable valve. The constituents of the offgas streams A1, A2.x, A3.y and A4 are varying amounts of hydrogen, inert gas, unreacted monomer or comonomer or vaporized suspension medium, with one or more constituents also being able to be present in only a very small amount or be completely absent.

Figures 2A, 2B, 2C and 2D schematically show how the offgas streams A1, A2.x, A3.y, A4 and A5 are processed according to the invention. The offgas streams A1, A2.x, A3.y and A4 are denoted by the same reference numerals which have been employed in figure 1. The reference numeral A5 denotes the total offgases which are obtained in the product work-up P, which is not shown in detail. In a vessel denoted by the reference numeral R5, all offgas streams A1, A2.x, A3.y, A4 and A5 are firstly combined and mixed. The vessel R5 can also, if required, take in additional gas streams of gaseous or vaporized monomer M or inert gas I from a possible compressor bypass from an upstream pressure stage.

From the vessel R5, the collected offgases are passed on via the line Q to the compression stage 10 and subsequently to the cooling stage 11 and from there go to the pressure vessel R6, which in the figure is provided with an external cooling jacket 12. The cooling stage 11 can comprise one or more cooling apparatuses by means of which stepwise cooling is possible. According to the invention, it is possible to set conditions in the pressure vessel R6 which are such that the individual components comonomer and vaporized suspension medium

present in the offgas streams A1, A2.x, A3.y, A4 and A5 are virtually completely liquefied. Thus, the offgases are, according to the invention, fractionated in the pressure vessel R6 to form a gaseous phase G1 which comprises most of the inert gas, hydrogen and monomer and a liquid phase L which comprises predominantly comonomer and suspension medium.

5 In a variant of the process of the invention shown in figure 2C, cooling of the compressed offgases can be carried out in a gas scrubber W by sprinkling with previously cooled, liquid phase. In this case, the liquid phase is circulated by means of the pump 13 and is cooled in the cooling stage 11. The pressure vessel R6 then serves as equalizing vessel for the liquid phase with the line S for first filling.

10 The gaseous phase G1 is recirculated continuously or discontinuously via regulatable valves (not shown) to the reactor R1 of the first reaction stage, while the liquid phase L is fed as total stream into one of the reactors R2.x or R3.y downstream of the first reactor R1. In a further variant of the invention, the liquid phase L can also be divided into substreams L2.x and L3.y and fed continuously or discontinuously into a plurality of reactors R2.x and R3.y.

15 In a further preferred variant of the process of the invention shown in figure 2B, the offgas stream A1 can be branched off separately from the circuit of the first reaction stage in reactor R1. The offgas stream A1 contains a particularly large proportion of hydrogen and inert gas and is particularly low in monomer and comonomer. This variant thus makes it possible to remove hydrogen and inert gas from the overall polymerization process in a targeted manner at 20 one point.

Figure 2D once again shows the preferred variant of the process of the invention using the gas scrubber W but without the offgas stream A1 from the first reactor R1.

25 The process of the present invention with circulation of the offgas makes it possible for the monomer and comonomer used to be utilized better, and the total yield of polymer, based on monomer and comonomer used, increases to a value above 98%, preferably up to 99.75%

Claims

1. A continuous process for preparing polyolefins having a bimodal or multimodal molar mass distribution in suspension in at least two reactors R1, R2.x, R3.y which are connected in series and in which different reaction conditions are set, wherein the offgases A1, A2.x, A3.y, A4 and A5 leaving all the reactors connected in series are collected, the collected offgases are then compressed in a compression stage 10, the compressed offgases are subsequently cooled and the cooled material is separated into a gaseous fraction and a liquid fraction and the separated fractions are then recirculated to the polymerization process at different points.
5
- 10 2. The process as claimed in claim 1, wherein the collected offgases A1, A2.x, A3.y, A4 and A5 are compressed to a pressure in the range from 0.5 to 2.5 MPa, preferably in the range from 0.9 to 2.0 MPa.
3. The process as claimed in claim 1 or 2, wherein the compressed offgases heat up to temperatures in the range from 30 to 250°C.
- 15 4. The process as claimed in one or more of claims 1 to 3, wherein the compressed offgases are cooled to a preferred temperature in the range from 0 to 100°C, particularly preferably in the range from 20 to 50°C.
5. The process as claimed in one or more of claims 1 to 4, wherein the cooled material separates at a pressure in the range from 0.5 to 2.5 MPa into a liquid phase L and a
20 gaseous phase G1 which are collected in a pressure vessel R6 and are then taken off separately from there.
- 25 6. The process as claimed in one or more of claims 1 to 5 which is carried out in the presence of a Ziegler catalyst, with the respective molar mass of the polymer fraction prepared in the various reactors R1, R2.x, R3.y and R4 being set by means of addition of hydrogen to the reaction mixture.
7. The process as claimed in one or more of claims 1 to 6, wherein the highest hydrogen concentration and the lowest comonomer concentration, based on the amount of monomer, is set in the first reactor R1 and the hydrogen concentration is gradually reduced and the comonomer concentration is gradually increased, in each case based on the amount of monomer used, in the downstream further reactors R2.x, R3.y and R4.
30

8. The process as claimed in one or more of claims 1 to 7, wherein ethylene or propylene is used as monomer and an alpha-olefin having from 4 to 10 carbon atoms is used as comonomer in an amount from 0 to 10% by weight, based on the total weight of the resulting polymer.
- 5 9. The process as claimed in one or more of claims 1 to 8, wherein a saturated hydrocarbon having from 4 to 12 carbon atoms or a mixture thereof is used as suspension medium.
10. The process as claimed in one or more of claims 1 to 9, wherein hydrogen and inert gas are removed from the overall polymerization process in a targeted manner at one point by the offgas stream A1 being branched off separately from the circuit of the other offgas streams A2.x, A.y, A4 and A5 of the first reaction stage in the reactor R1, with the offgas stream A1 comprising a particularly large proportion of hydrogen and inert gas and being particularly low in monomer and comonomer.

Abstract

The invention relates to a continuous process for preparing polyolefins having a bimodal or multimodal molar mass distribution in suspension in at least two reactors R1, R2.x, R3.y which are connected in series and in which different reaction conditions are set. In this process, 5 the offgases A1, A2.x, A3.y, A4 and A5 leaving all the reactors connected in series are firstly collected, the collected offgases are then compressed in a compression stage 10, the compressed offgases are subsequently cooled and the cooled material is separated into a gaseous fraction and a liquid fraction. The separated fractions are then recirculated to the polymerization process at different points. The process of the invention allows the total conversion of the polymerization, 10 based on monomer and comonomer used, to be increased to a surprising extent.

FIG.1

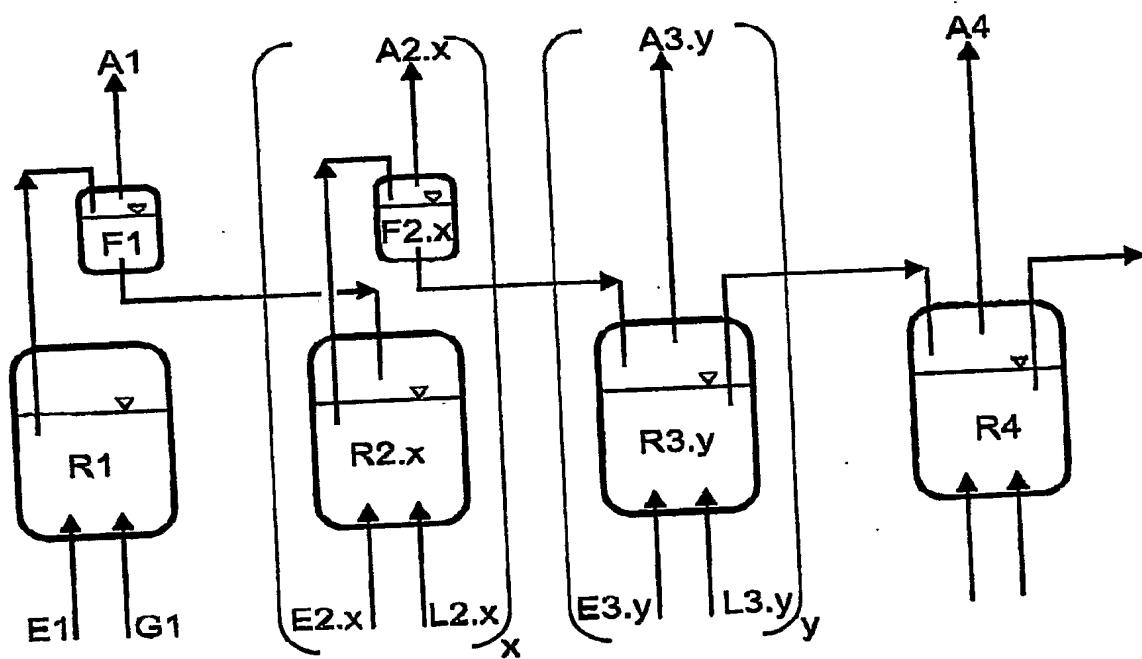


FIG.2A

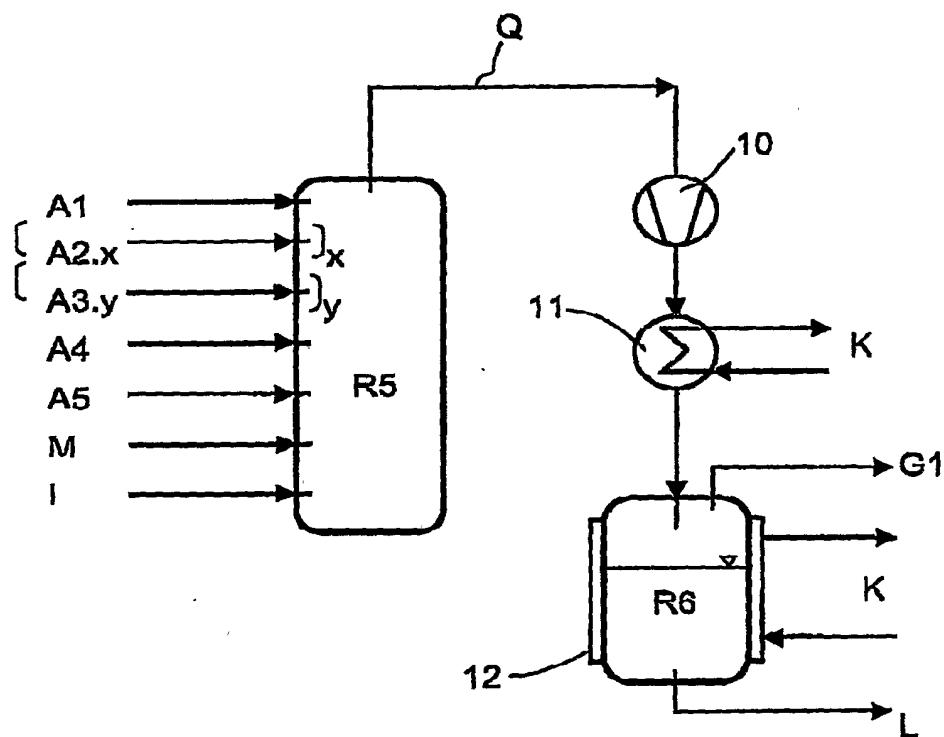


FIG.2B

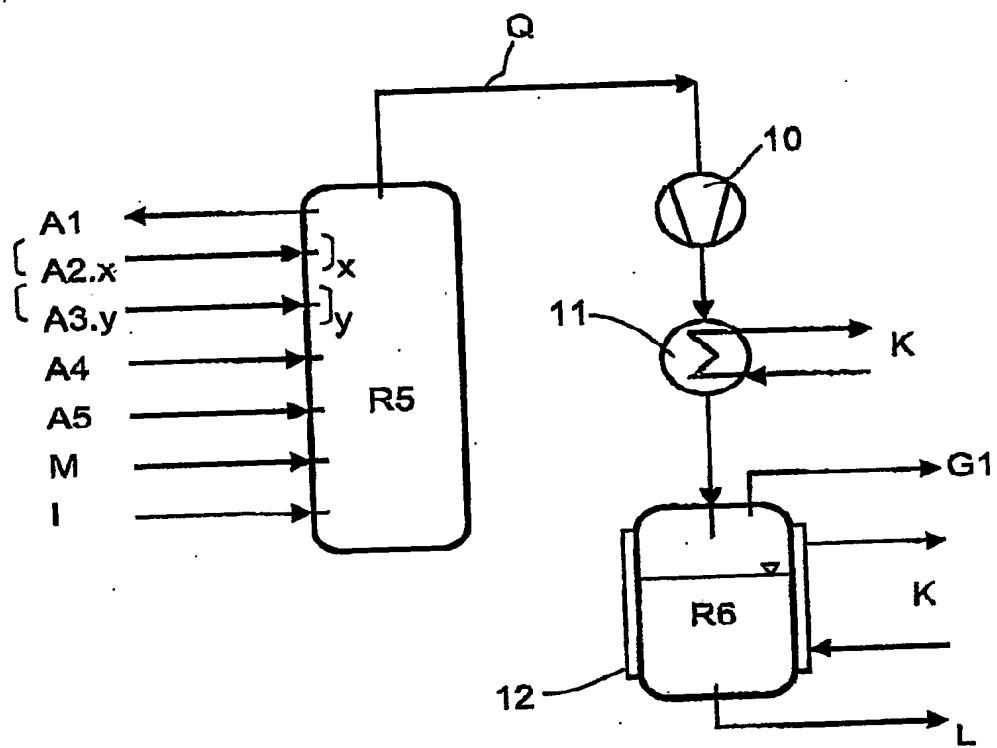


FIG.2C

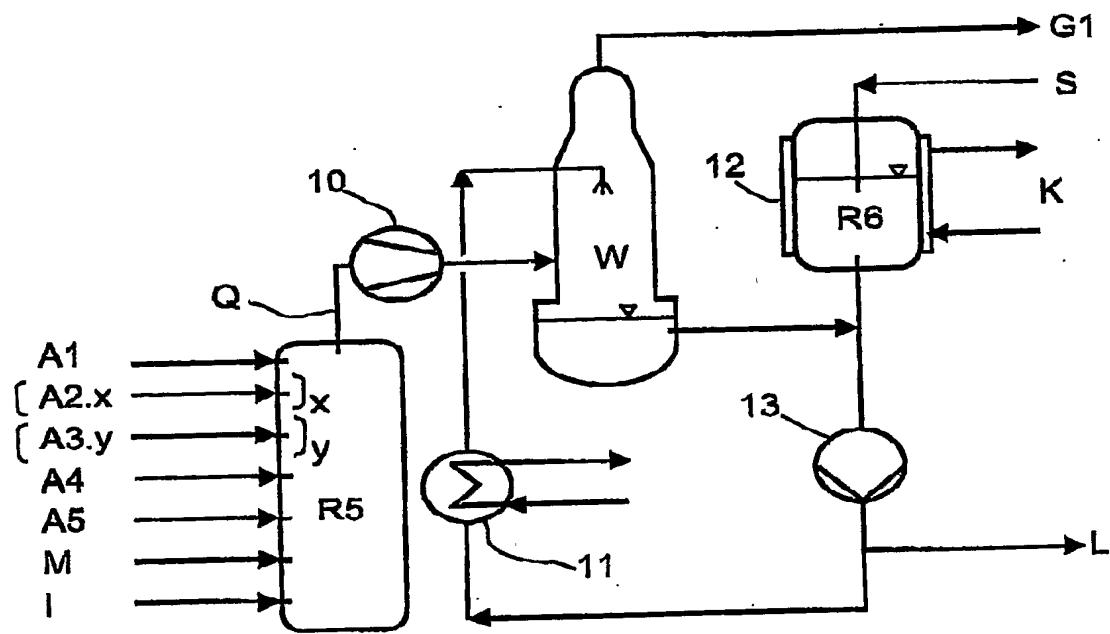


FIG.2D

